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# Catalysis and Organometallic Chemistry of Rhodium and Iridium in the Oxidation of Organic Substrates

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**Abstract** The purpose of this chapter is to present a survey of the organometallic chemistry and catalysis of rhodium and iridium related to the oxidation of organic substrates that has been developed over the last 5 years, placing special emphasis on reactions or processes involving environmentally friendly oxidants. Iridium-based catalysts appear to be promising candidates for the oxidation of alcohols to aldehydes/ketones as products or as intermediates for heterocyclic compounds or domino reactions. Rhodium complexes seem to be more appropriate for the oxygenation of alkenes. In addition to catalytic allylic and benzylic oxidation of alkenes, recent advances in vinylic oxygenations have been focused on stoichiometric reactions. This review offers an overview of these reactions

as well as some comments on key questions related to achieving the desired C – O bond formation.

**Keywords** Rhodium · Iridium · Catalysis · Oppenauer-type oxidations · Allylic oxygenations · Oxetanes · Dioxolanes · N-based ligands · Dioxygen · Hydrogen peroxide

## 1 Introduction

Oxidation of organic compounds is a basic tool in chemistry, covering a broad spectrum of stoichiometric and catalytic reactions ranging from the production of bulk chemicals to chiral compounds in which enantioselectivity is of particular importance. However, oxidation reactions yielding valuable products from organic raw materials are one of the most problematic transformations, although they constitute industrial core technologies. In particular, converting the basic materials of the industry, olefins and hydrocarbons, into oxygenated species such as alcohols, diols, epoxides, and carbonyl compounds is of general importance [1]. Moreover, the current main challenge and the goal in oxidation is to carry out these reactions with no waste and using environmentally friendly oxidants such as oxygen [2] or hydrogen peroxide [3, 4], which require new, selective, and efficient catalytic processes.

The most widely developed catalytic methods in oxidation involve complexes of the early and middle transition metals, generally in high-oxidation state and some late transition metals such as palladium and copper [5], but this is a wide field and under continuous development [6]. Rhodium and iridium compounds are less known as oxygenation catalysts than other metals, although their ability to form dioxygen complexes and their use as hydrogen transfer catalysts has been known of for a long time [7, 8]. However, after promising initial reports in the 1980s and early 1990s, they were then overlooked until quite recently when new results began to appear.

In this chapter we describe recent developments in the catalytic dehydrogenation of alcohols and related reactions as well as the organometallic chemistry of rhodium and iridium based on the oxygenation of coordinated alkenes.

# 2
# Catalytic Oxidations Based on Rhodium and Iridium

## 2.1
## Historical Background

### 2.1.1
### Oxygenation of C = C Bonds

Most of the catalytic studies on the oxygenation of alkenes were carried out in the 1970s and 1980s in which typical rhodium complexes [9, 10] such as $[RhCl(PPh_3)_3]$ [11], or even $Rh^{III}Cl_3$ [12–14] with or without co-catalysts ($Cu^{II}$ [14, 15] or $Bi^{III}$ [16]), and some iridium compounds such as $[\{Ir^{III}(\mu\text{-}Cl)HCl(cod)\}_2]$ [17] were used as catalyst precursors.

Rhodium complexes were generally found to be more effective than iridium, but on the whole they show moderate activity in alkene oxygenation reactions. Significantly, epoxides, a typical product of the oxidation of olefins catalyzed by the middle transition metals, have rarely been evoked as products [18–22]. Although allylic alcohols [23] or ethers [24] have sometimes been described as products, the above cited rhodium and iridium complexes are characterized by an excellent selectivity in the oxygenation of terminal alkenes to methyl ketones.

With the exception of the binary system $RhCl_3/Cu(ClO_4)_2$ [9, 24], which incorporates the two atoms of dioxygen to the substrate (dioxygenase activity) (Eq. 1) all the rest show monooxygenase activity, incorporating only one oxygen atom to the substrate.

$$2\ R\text{-}CH{=}CH_2 + O_2 \xrightarrow[EtOH,\ 20 - 80^{\circ}\ C]{RhCl_3 + Cu(ClO_4)_2} 2\ R\text{-}CO\text{-}CH_3$$

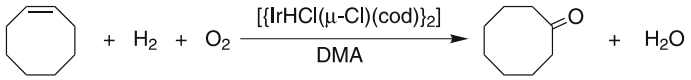
**Equation 1**

The second oxygen atom is trapped either by $PPh_3$ to $OPPh_3$ [11] (Eq. 2a), or with $H_2$ to $H_2O$ [25] (Eq. 2b), or more commonly by alcohols [26] that behave as two hydrogen donors to give $H_2O$ and the corresponding aldehyde/ketone (Eq. 2c).

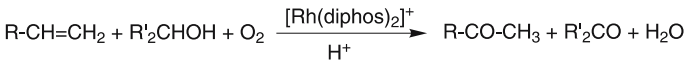
From a mechanistic point of view, the behavior of these catalysts represents a complicated puzzle [27], still poorly understood today, in which the original proposed catalytic cycles reveal several critical points in the light of present

$$R\text{-}CH{=}CH_2 + PPh_3 + O_2 \xrightarrow{[RhCl(PPh_3)_3]} R\text{-}CO\text{-}CH_3 + OPPh_3$$

**Equation 2a**

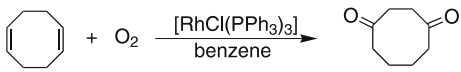



**Equation 2b**

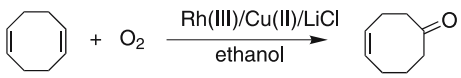



**Equation 2c**

knowledge on rhodium and iridium chemistry, covered by an excellent review by de Bruin [28]. Moreover, similar substrates give different products depending on the conditions, so that more than one single mechanism, that is still unclear, could be operative. For example, 1,5-cyclooctadiene (cod) can be oxygenated either to 1,4-cyclohexadione (Eq. 3a) [29] or to 4-cyclohexenone (Eq. 3b) [16].




**Equation 3a**

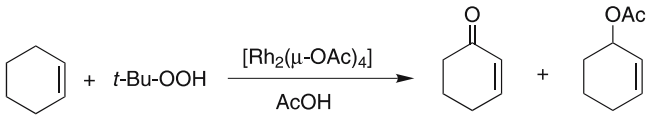



**Equation 3b**

On the whole, all proposed mechanisms contain three relevant steps: (1) coordination of the olefin and oxygen, (2) C – O bond formation, (3) elimination of the ketone with regeneration of the catalytically active species. In recent years, rather than searching for new catalytic systems based on rhodium and iridium compounds, attention has been focused on understanding the organometallic chemistry involved in the oxygenation of C = C bonds, as described in Sect. 3.

### 2.1.2 Allylic Oxygenation

Although the catalytic reactions described above involve mononuclear $Rh^{I}$ and $Rh^{III}$ complexes, dinuclear $Rh^{II}$ compounds have also been studied as catalyst precursors in oxygenation reactions. The system $[Rh_2(\mu\text{-}OAc)_4]$/*t*-BuOOH is effective in the oxidation of cyclic alkenes such as cyclopentene, cyclohexene and cycloheptene, mainly to $\alpha,\beta$-unsaturated ketones and allylic acetates, but with poor yields (Eq. 4) [30, 31].



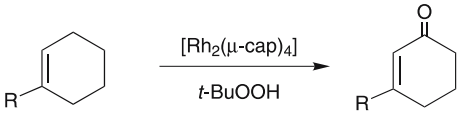

**Equation 4**

The mechanism operating in these reactions seems to follow a radical path that could be related to the classic Haber-Weiss radical-chain sequence [32] based on the couple $[Rh_2^{II}(\mu\text{-}OAc)_4]/[Rh_2^{II,III}(\mu\text{-}OAc)_4]$.

## 2.2
## Allylic and Benzylic Oxygenation of Alkenes

The low effectiveness of the $[Rh_2^{II}(\mu\text{-}OAc)_4]$ system [31] in the oxygenation of alkenes has been attributed to its high oxidation potential to form the mixed-valence complex $[Rh_2^{II,III}(\mu\text{-}OAc)_4]$ on the basis of a relationship between the ability of the complexes to transfer one electron and the effectiveness of the catalysts in allylic oxidation, suggested by Kochi [33].

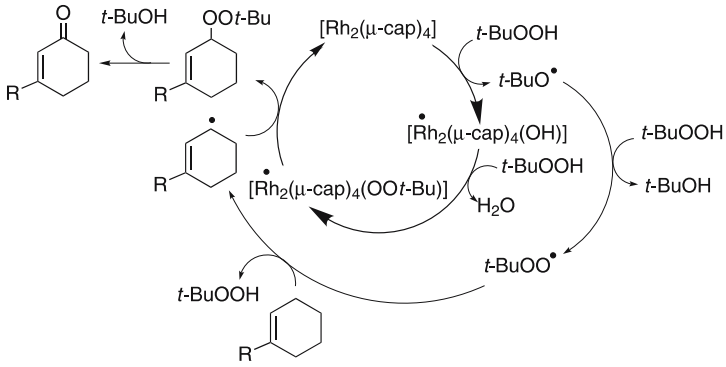
The related dirhodium(II) $\alpha$-caprolactamate (cap) complex $[Rh_2(\mu\text{-cap})_4]$ undergoes a one-electron oxidation process at quite a lower potential (11 mV) than the acetate complex (1170 mV). In agreement with the Kochi hypothesis, the $\alpha$-caprolactamate complex has recently been found to be an exceptional catalyst for the allylic oxidation of alkenes under mild conditions. A wide range of cyclohexenes, cycloheptenes, and 2-cycloheptenone (Eq. 5) are rapidly converted to enones and enediones in 1 h with only 0.1 mol % of $[Rh_2(\mu\text{-cap})_4]$ and yields ranging from 60 to 90%, in the presence of potassium carbonate [34].



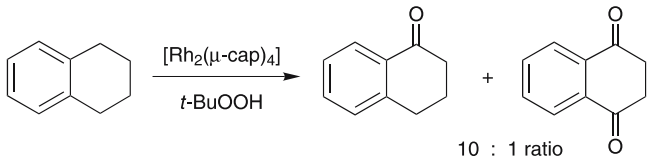

**Equation 5**

The proposed mechanism (Scheme 1) involves the mixed-valence compounds $[Rh_2^{II,III}(\mu\text{-cap})_4(OH)]$ and $[Rh_2^{II,III}(\mu\text{-cap})_4(OO\textit{t}\text{-Bu})]$ formed from the homolytic cleavage of *t*-BuOOH. The *t*-BuOO$^{\cdot}$ radicals in the medium promote a selective hydrogen abstraction from the alkene to give the allylic alkenyl radical. This species traps the peroxide in $[Rh_2^{II,III}(\mu\text{-cap})_4(OO\textit{t}\text{-Bu})]$ to produce the alkenyl hydroperoxide, which rapidly decomposes to the isolated products, thus regenerating the catalyst.

This system also catalyzes the benzylic oxidation of 1,2,3,4-tetrahydronaphthalene [35] (Eq. 6) and hydrocarbons containing benzyl groups with




**Scheme 1**




**Equation 6**

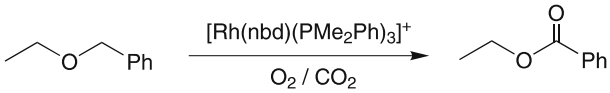
yields of up to 99% in 16 h in the presence of sodium hydrogencarbonate as base.

Moreover, this catalyst is also effective in the oxidation of a spirocyclic acetal of 5-methoxy-1,2,3,4-tetrahydronaphthalenone to palmarumycin $CP_2$ [35], a biosynthetic precursor to the preussomerin class of natural products exhibiting a wide range of biological activity.

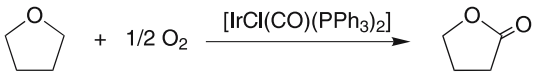
## 2.3 Oxidation of Ethers

The cationic complex $[Rh(nbd)(PMe_2Ph)_3](BF_4)$ catalyzes the oxygenation of several ethers (Eq. 7) by $O_2/CO_2$ mixtures with moderate turnovers (1,000 in 8 days at 60 °C for $\gamma$-butyrolactone) [36], accompanied by the reduction of $CO_2$ to formic acid. In the absence of $CO_2$, 2-hydroperoxidetetrahydrofuran is the major product.

More recently, Vaska's compound $[IrCl(CO)(PPh_3)_2]$, was found to be a better catalyst than the cationic rhodium complex in the oxidation of THF




**Equation 7**

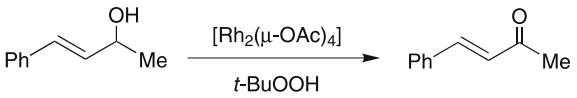



**Equation 8**

to $\gamma$-butyrolactone (Eq. 8) under ambient conditions with a TON (turnover number) of 150 in 48 h, along with 4-hydroxybutyraldehyde [37].

## 2.4 Oxidation of Alcohols

Recent advances in alcohol oxidations by rhodium and iridium complexes have mainly focused on Oppenauer-type oxidations or reactions in which this type of oxidation is an intermediate step. An independent result is the oxidation of allylic (Eq. 9) and benzylic alcohols with *t*-BuOOH to the corresponding $\alpha,\beta$-unsaturated ketones [38] with $[Rh_2(\mu\text{-}OAc)_4]$. The reactions were carried out at room temperature in dichloromethane and yields of up to 92% (by GC) in 24–48 h have been described.




**Equation 9**

### 2.4.1 Simple Oppenauer-type Oxidations

For a long time, rhodium and iridium complexes have been known to be highly effective homogeneous catalysts for hydrogen-transfer reactions. Initially, they were used to promote hydrogen transfer from isopropanol to organic substrates in hydrogenation reactions giving acetone [39, 40]. The hydrogen transfer reaction has been also used for the hydrogenation of ketones to alcohols (Eq. 10) [41, 42].

Since these are chemical equilibrium reactions, by modifying the reaction conditions, i.e., using acetone as solvent instead of isopropanol, the reaction can be reversed, and therefore used for the oxidation (dehydrogenation) of alcohols (Oppenauer-type oxidation) [43]. Moreover, since acetone is the hy-


**Equation 10**

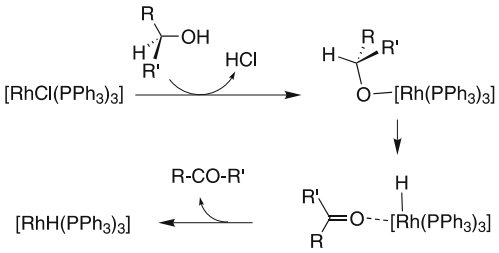
drogen acceptor the reactions are carried out in an environmentally benign fashion.

The mechanism operating in rhodium-catalyzed and iridium-catalyzed hydrogen transfer reactions involves metal hydrides as key intermediates. Complexes such as $[\{M(\mu\text{-}Cl)(L_2)\}_2]$, $[M(cod)L_2](BF_4)$ (M = Rh, Ir; $L_2$ = dppp, bipy), and $[RhCl(PPh_3)_3]$ are most likely to follow the well-established mechanism [44] via a metal alkoxide intermediate and $\beta$-elimination to generate the active hydride species, as shown in Scheme 2.

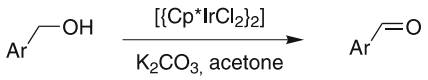
The system $[\{Ir(\mu\text{-}Cl)Cp^*Cl\}_2]/K_2CO_3$ [45, 46] was recently reported to be a catalyst for the oxidation of primary (Eq. 11) and secondary alcohols to the corresponding carbonyl compounds in acetone.

The catalytic cycle starts with the formation of the metal alkoxide complex with the removal of the hydrogen chloride generated in this step by the base. The base ($K_2CO_3$ in this case) is indeed necessary to enhance catalytic activity in this system. For example, benzyl alcohol is oxidized to benzaldehyde with a 13% conversion in the absence of $K_2CO_3$, while the conversion rises to 71% after $K_2CO_3$ addition. The aldehyde is then produced via $\beta$-hydride elimination from the alkoxide to give an iridium hydride complex, which inserts acetone into the Ir – H bond to give the isopropoxide complex. Protonation of isopropoxide by the alcohol releases isopropanol and regenerates the alkoxide complex [46].

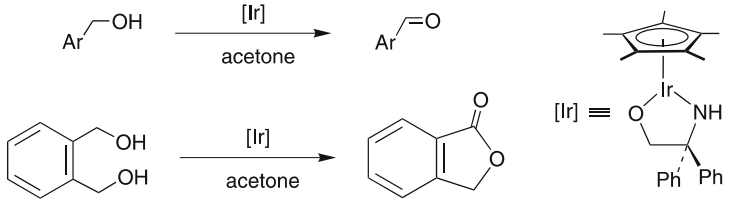
The variety of complexes containing the "IrCp*" moiety allows the fine-tuning of the catalyst's properties to enhance selectivities by a careful choice of the remaining ligands. The incorporation of doubly deprotonated aminoalcohols into the "IrCp*" moiety gives neutral complexes, such as $[IrCp^*(OCH_2CPh_2NH)]$ with the N,O based bifunctional ligand (Scheme 3) [47]. This catalyst is also active for the oxidation of alcohols and for the oxidative lactonization of 1,4 or 1,5-diols [48], using acetone




**Scheme 2**




**Equation 11**




**Scheme 3**

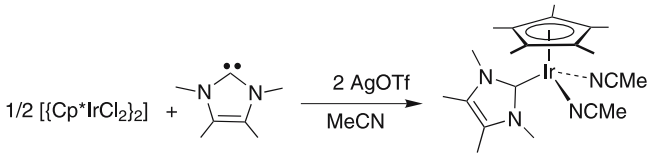
as the hydrogen acceptor (Scheme 3). Similar complexes containing chiral aminoalcoholates as ligands have shown a good activity for the asymmetric lactonization of several meso-diols [49] to afford the corresponding lactones in a yield of up to 81 ee and 99%.

More recently, it was found that the incorporation of N-heterocyclic carbene ligands to the "Cp*Ir" moiety (Eq. 12) considerably enhances catalyst activity for alcohol oxidation reactions [50, 51]. By way of example, the oxidation of secondary alcohols occurs with high turnovers, up to 3,200 for the oxidation of 1-phenylethanol and 6,640 for that of cyclopentanol (95% yield, 40 °C, 4 h) using the complex with the carbene derived from the tetramethylimidazole (Eq. 12).

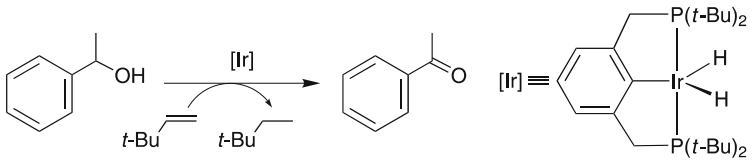
This enhancement could be attributed to an increase in the nucleophilicity of the iridium-hydride intermediate, due to the good electron donor ability of this type of ligand, which leads to the acceleration of the hydride transfer to acetone as the hydrogen acceptor.

An interesting case of heterobimetallic catalysis occurs with the complex $[(\eta^5\text{-}C_5Ph_4O)Rh(\mu\text{-}Cl)_3Ru(PPh_3)_2(Me_2CO)]$, which is an efficient catalyst for the oxidation of both primary and secondary alcohols under mild conditions. The cooperation of two metals in this homogeneous bimetallic-catalysis is noteworthy since the homometallic complexes $[\{Rh(\mu\text{-}Cl)(\eta^5\text{-}C_5Ph_4O)\}_2]$ and $[(PPh_3)_2ClRu(\mu\text{-}Cl)_3Ru(PPh_3)_2(Me_2CO)]$ were ineffective for the Oppenauer oxidation [52].

Water-soluble catalysts for Oppenauer-type oxidation of alcohols can be achieved by adding functionalized salts of classical ligands such as dipotassium 2,2′-biquinoline-4,4′-dicarboxylate (BQC) to acetone-water mixtures. In this way, the catalyst system $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$/BQC is highly efficient for the selective oxidation of a wide range of alcohols such as benzylic,




**Equation 12**




**Equation 13**

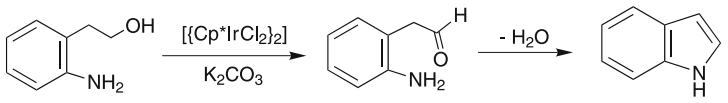
1-heteroaromatic, allylic, and aliphatic secondary alcohols to the corresponding ketones using catalyst/substrate ratios ranging from 0.4 to 2.5% and yields up to 87% in 4 h [53, 54].

A related dehydrogenation of primary and secondary alcohols to the corresponding aldehydes/ketones has been achieved using the dihydride iridium compound $[IrH_2(C_6H_3\text{-}2,6\{CH_2P\text{-}t\text{-}Bu_2\}_2)]$ as the precursor's catalyst and *t*-butylethylene as hydrogen acceptor (Eq. 13). The reactions are carried out at 200 °C with a 99% yield in 18 h (alcohol/Rh = 10/1) [55].

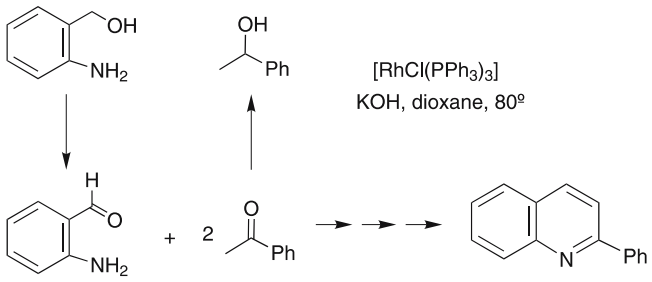
A plausible mechanism involves the reaction of the dihydride precursor with *t*-butylethylene to the 14-e complex $[Ir(C_6H_3\text{-}2,6\{CH_2P\text{-}t\text{-}Bu_2\}_2)]$, which undergoes the oxidative-addition reaction of the alcohol to afford a hydride alkoxide complex. Further $\beta$-hydride elimination gives the aldehyde/ketone and regenerates the dihydride active species [55]. In the particular case of 2,5-hexanediol as the substrate, the product is the cyclic ketone 3-methyl-2-cyclopenten-1-one. The formation of this ketone involves the oxidation of both OH groups to 2,5-hexanedione followed by an internal aldol reaction and further oxidation as in the final step of a Robinson annulation reaction [56].

### 2.4.2
### Oxidation and Cyclisation: Synthesis of Indoles and Quinolines

Starting from *ortho*-aminoalcohols as substrates, the products are indoles (Eq. 14) resulting from the condensation of the aldehyde and the amino group. This reaction is catalyzed by the system $[\{Ir(\mu\text{-}Cl)Cp^*Cl\}_2]/K_2CO_3$ in toluene. This catalyst was also efficient for the synthesis of 1,2,3,4-tetrahydroquinolines and 2,3,4,5-tetrahydro-1-benzazepine [57] starting from the corresponding aminoalcohols. Since the reactions are carried out in toluene, a protonation of the iridium hydride by the alcohol with removal of hydrogen has been suggested to regenerate the iridium alkoxide species [57].




**Equation 14**




**Scheme 4**

Quinolines can be prepared from the oxidative coupling and cyclation of the 2-aminobenzyl alcohol and ketones (Scheme 4) catalyzed by the system $[RhCl(PPh_3)_3]$/KOH [58]. The reactions were carried out in dioxane at 80 °C with 85% yield in 24 h (alcohol/Rh = 100/1). However, better yields are obtained with the related ruthenium system $[RuCl_2(=CHPh)(PCy_3)_2]$ [59].

In this case, the 2-aminobenzyl alcohol is oxidized to 2-aminobenzaldehyde, which undergoes an aldol condensation with the ketone to give an $\alpha,\beta$-unsaturated ketone. This is followed by cyclodehydratisation to form quinoline. An excess of ketone is necessary to act as a sacrificial hydrogen acceptor.

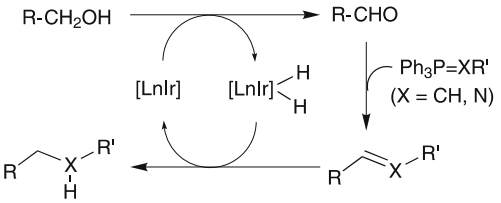
### 2.4.3 Domino Reactions

A recent methodology for the synthesis of organic compounds uses the oxidation of alcohols to aldehydes [60] as the first step in a three-step domino reaction sequence to attach the carbon chain of the alcohol to alkanes, amines or ketones. The second step is the well-known condensation of the carbonyl compound with a Wittig reagent, aza-Wittig or amines, and methylketones to give alkenes, imines, and $\alpha,\beta$-unsaturated ketones, respectively. Finally, these unsaturated compounds are reduced by hydrogen transfer reactions using the same catalyst introduced for the oxidation of the alcohol. Coupling these three reactions in a one-pot reaction directly affords the products.

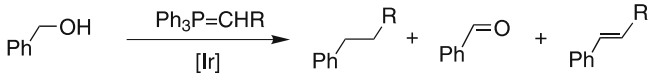
Scheme 5 shows a formal explanation of this conceptual idea for alkanes developed by Williams [60]: the alcohol is first oxidized into the aldehyde affording a hydride complex. The aldehyde is then condensed with the Wittig reagent to form the unsaturated compound, which becomes hydrogenated by the hydride complex, thus regenerating the catalyst.

The catalyst for this type of reaction was $[\{Ir(\mu\text{-Cl})(cod)\}_2]$/dppp/$Cs_2CO_3$. For the reaction shown in Eq. 15, a 100% conversion with selectivities of 80% in alkane, 5% in aldehyde and 12% in alkene were obtained for R = COOBn.

An extension of this methodology [61] to amines instead of alkanes, using the same catalyst precursor, is obtained by replacing the Wittig reagent,



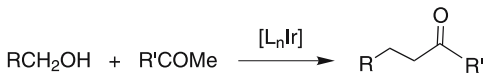

**Scheme 5**




**Equation 15**

$PPh_3P = CHR$, with the aza-analogue $PPh_3P = NR$ (Scheme 5). The condensation of the aldehyde, generated "in situ", with $PPh_3P = NR$ gives the imine, which was hydrogenated to the amine.

A related process, from this conceptual point of view (Eq. 16), the use of the aldehyde generated "in situ" for further reactions, has allowed the $\alpha$-alkylation of ketones with primary alcohols [62]. Several ketones have been condensed with 1-butanol or benzyl alcohol affording the corresponding $\alpha$-alkylated ketones in good yields (up to 96%) in the presence of $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$ and KOH.




**Equation 16**

This method is a very convenient route to obtain aliphatic ketones because the carbonyl function can be placed in the desired position by selecting the ketones and alcohols employed.

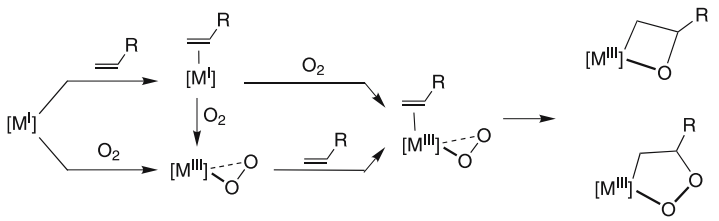
The N-alkylation of amines with alcohols [63] can also be carried out with $Ir^{III}$ catalysts through a similar domino sequence reaction. In this case, the aldehyde/ketone resulting from oxidation is condensed with an amine to the corresponding imine, which is hydrogenated to the alkylated amine [63]. By way of example, the reaction of benzyl alcohol with aniline in toluene afforded benzylaniline in a 88% isolated yield by using catalytic amounts of $[\{Ir(\mu\text{-}Cl)Cp^*Cl\}_2]/K_2CO_3$.

# 3
# Organometallic Chemistry of Rhodium and Iridium Directed towards Olefin Oxygenation

Most of the recent studies on the stoichiometric oxygenation of C = C bonds coordinated to rhodium and iridium focus on the search for suitable precursors able to promote the desired C – O bond formation reaction between the carbon of the olefin and the oxygen from the oxygen source, typically dioxygen or hydrogen peroxide. Prototype complexes with the "$M^{I}$(olefin)" framework along with di-, tri- and tetradentate N-based ligands are commonly used for two reasons: (1) the well-known changes in the hapticity of these ligands that allow coordination vacancies to be generated if necessary, and (2) their resistance to oxidation, which is clearly greater than that of posphane ligands. Up to now, ligands with hard donor atoms of the main groups (N, O) seem to create the more appropriate metal environments for the oxidation of olefins. Nevertheless, this is a feature that requires further study, and close observation of the properties of organometallic compounds by practitioner chemists to recognize chemical oxidations.

## 3.1
## Reactions with Dioxygen

The olefin oxygenations carried out with dioxygen seem to be metal-centered processes, which thus require the coordination of both substrates to the metal. Consequently, complexes containing the framework "$M^{III}$(peroxo)(olefin)" represent key intermediates able to promote the desired C – O bond formation, which is supposed to give 3-metalla$^{III}$-1,2-dioxolane compounds (Scheme 6) from a 1,3-dipolar cycloinsertion. This situation is quite different from that observed in similar reactions involving middle transition metals for which the direct interaction of the olefin and the oxygen coordinated to the metal, which is the concerted oxygen transfer mechanism proposed by Sharpless, seems to be a more reasonable pathway [64] without the need for prior olefin coordination. In principle, there are two ways to produce the "$M^{III}$(peroxo)(olefin)" species, shown in Scheme 6, both based on the easy switch between the $M^{I}$ and $M^{III}$ oxidation states for

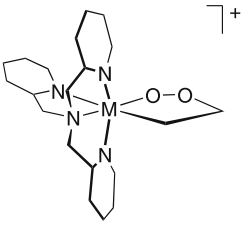



**Scheme 6**

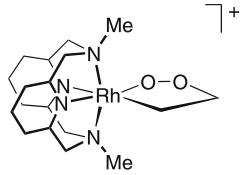
rhodium and iridium. The first possibility seems to be the most plausible since it combines the ability of these metals in low oxidation state to coordinate olefins with a feasible further oxidation to the desired species, although the simple replacement of the olefin by dioxygen could also be a possible competitive reaction. The second possibility involves the coordination of the olefin to a "$M^{III}$(peroxo)" complex, but given the low affinity of these metals in the $M^{III}$ oxidation state for olefins, and the inertness of these compounds, this possibility seems to be less likely, although it could be an equilibrium operative for catalytic processes.

### 3.1.1
### Solid-gas Reactions to 3-metalla$^{III}$-1,2-dioxolane Complexes

Compounds of the 3-metalla$^{III}$-1,2-dioxolane type were unknown in rhodium and iridium chemistry until 2001 [65] when Gal reported the preparation of some examples through solid-gas reactions, quite an uncommon type of chemistry. They were initially obtained from the cationic complex [Rh($\kappa^4$-tpa)($C_2H_4$)]$^+$ (tpa = *N*,*N*,*N*,-tris(2-pyridylmethyl)amine), and then extended to the iridium counterparts and the rhodium [66] compounds [Rh($\kappa^4$-dpda-$Me_2$)($C_2H_4$)]$^+$ (Fig. 1) (the aromatic circles for the pyridine rings have been omitted for clarity).




[M(κ$^4$-tpa)(κ$^2$-$O_2C_2H_4$)]$^+$



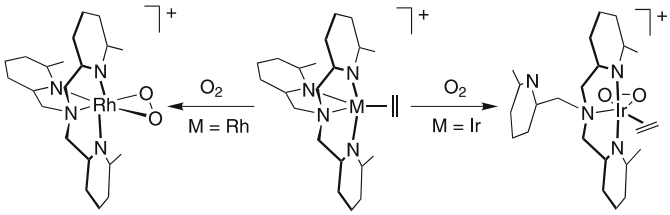

[Rh(κ$^4$-dpda-$Me_2$)(κ$^2$-$O_2C_2H_4$)]$^+$

**Fig. 1**

These solid-gas reactions represent, at the moment, the single path to 3-metalla$^{III}$-1,2-dioxolane complexes of rhodium and iridium. Complexes of this type have been widely proposed in catalytic cycles. However, it is unlikely that they take part in oxygenations with rhodium because of their high reactivity (see below) and the special conditions for their preparation.

### 3.1.2
### Reactions in Solution to Peroxo Complexes

Reactions of the above-mentioned ethylene derivatives with dioxygen *in solution* afford mixtures of uncharacterized compounds [67] with minor ex-




**Scheme 7**

ceptions. For example, the "$Rh^{III}$peroxo" complex $[Rh(\kappa^4\text{-}Me_3tpa)(O_2)](PF_6)$ ($Me_3tpa$ = *N*,*N*,*N*-tris[(6-methyl-2-pyridyl)methyl]amine) was obtained in quantitative yield after the clean replacement of ethylene in $[Rh(\kappa^4\text{-}Me_3tpa)(C_2H_4)]$ by dioxygen (Scheme 7) [68]. The iridium counterpart coordinates $O_2$ without ethylene replacement, to give an "$Ir^{III}$(peroxo)(ethylene)" compound, $[Ir(\kappa^3\text{-}Me_3tpa)(O_2)(C_2H_4)](PF_6)$ (Scheme 7) in a rather low yield. The incoming of the new ligand is associated with a change in the coordination mode of the ligand from $\kappa^4$ to $\kappa^3$ [68]. In these reactions, the regioselectivity of the reactions is driven by the nature of the metal.

The iridium complex models one of the proposed intermediates in the catalytic conversion of alkenes to ketones, but the expected C – O bond formation reaction is not observed. A related example in rhodium chemistry, $[RhH(O_2)\{CH_2 = C(CH_2CH_2Pt\text{-}Bu_2)_2\}]$ (Fig. 2) [69], is the only complex in which a peroxide ligand coexists with an olefin moiety, which forms part of the pincer ligand. The lack of C – O bond formation in both complexes could be indicative of a stereochemical requirement or a "further activation" of oxygen for the mentioned coupling, which is not accessible in these complexes. In fact, both show a similar arrangement of the peroxide and the C = C bond in the solid state, both being coplanar and forming a bow tie with the metal, in which the C = C and O – O edges are almost parallel.

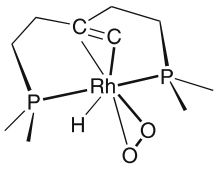



**Fig. 2**

Thus, although the coordination of the olefin and the dioxygen at the same metal center seems to be a required condition for achieving oxygen transfer, it does not seem to be the only one.

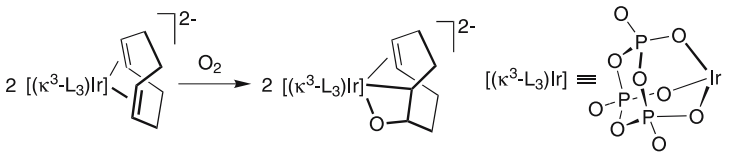
### 3.1.3
### Reactions in Solution to 2-metalla$^{III}$oxetanes

Rhodium and iridium complexes incorporating diolefins such as 1,5-cyclooctadiene (cod) are more reluctant to react with molecular oxygen than the ethylene analogues. To date, only two cod compounds, [Ir($\kappa^3$-$P_3O_9$)(cod)](TBA)$_2$ and [Rh($\kappa^2$-PhN$_3$Ph)(cod)] react straightforwardly with dioxygen under mild conditions. The result of the reactions is a mononuclear 2-irida$^{III}$oxetane-type complex in the case of iridium (Eq. 17) [70], while for rhodium the related 2-rhoda$^{III}$oxetane complex (Scheme 8) is dinuclear [71]. In both reactions all the oxygen consumed is incorporated in the substrate, thus yielding a 100% atom-economy processes.

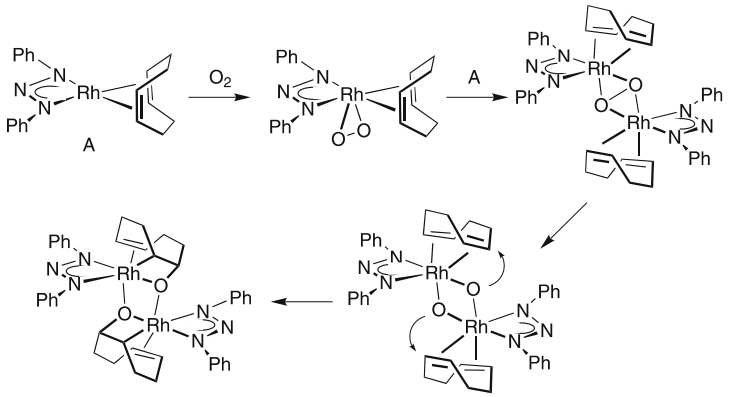
The structure of the rhodium compound and the kinetic study of the reaction provide strong evidence of a binuclear activation of dioxygen with complete effective transfer of both oxygen atoms to C = C bonds.

According to the second order of the reaction, the rate-determining step is the formation of a "Rh$^{III}$(peroxo)(cod)" complex from [Rh($\kappa^2$-PhN$_3$Ph)(cod)] and dioxygen. This peroxo compound undergoes the attack of an intact molecule of [Rh($\kappa^2$-PhN$_3$Ph)(cod)] to complete the dinuclear oxygen cleavage with the formation of two C – O bonds.

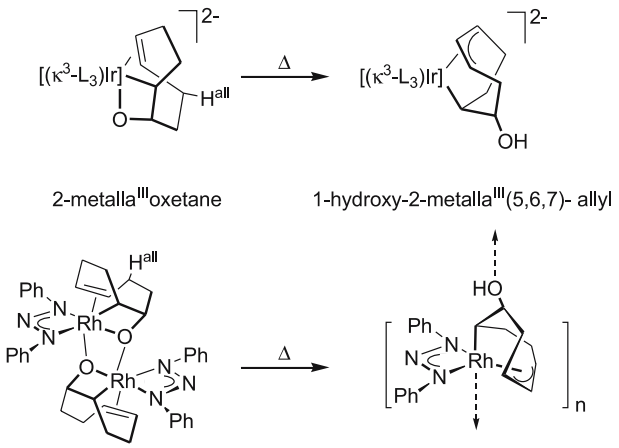
Probably, the key to the insertion of each oxygen atom in a C = C bond lies in the characteristics of the proposed intermediate "Rh$_2$($\mu$-oxo)$_2$" com-




**Equation 17**




**Scheme 8**




**Scheme 9**

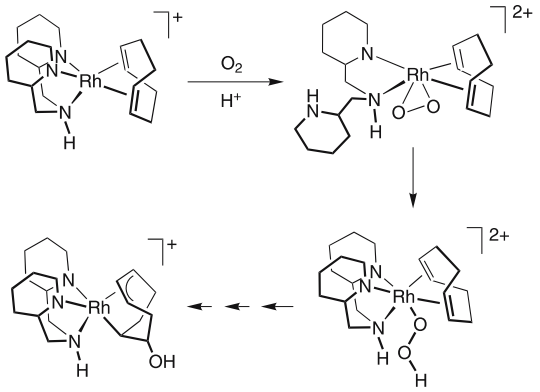
plex. Thus, the coordination of the second metal to the peroxo ligand cleaves the O – O bond and each oxide ligand is transferred to the closest C = C bond. The most relevant aspect of these two 100% atom economy reactions is a strong indication of the existence of an effective dinuclear pathway to activate dioxygen that produces C – O bonds without waste, which is available for the late transition metals in a relatively low oxidation state.

These two 2-metalla$^{III}$oxetanes are the isolated kinetic products of the reactions, which transform into 1-hydroxy-2-metalla$^{III}$(5,6,7)-allyl derivatives through the migration of a proton from the methylene group, specified in Scheme 9, to the oxygen. The regioselectivity of this isomerisation indicates a preference for the activation of the C – H bond at this site through a common yet unknown way. The distinct hapticity of the ancillary ligand in both cases determines the iridium complex to be mononuclear, while the corresponding rhodium system is polymeric in the solid state.

### 3.1.4
### Acid-catalyzed Reactions to 1-hydroxy-2-rhoda$^{III}$(5,6,7)-allyl Derivatives

The typical reluctance of the cod derivatives to react with dioxygen has been overcome, in some cases, by different approaches. Using catalytic amounts of acid [72], the otherwise inert complex [Rh($\kappa^3$-bpa)(cod)]($PF_6$) reacts with oxygen to give the 1-hydroxy-2-rhoda$^{III}$(5,6,7)-allyl derivative [Rh($\kappa^3$-bpa)($C_8H_{11}OH$)]($PF_6$) (Scheme 10) with a consumption of one mole of $O_2$ per mol of [Rh($\kappa^3$-bpa)(cod)]($PF_6$), i.e., it is a 50% atom-economy process.

Probably, the acid protonates one of the pyridine rings to give the 16 electron-valence complex [Rh($\kappa^2$-bpaH)(cod)]($PF_6$)$_2$. This complex can then react with molecular oxygen to give an "Rh$^{III}$(peroxo)(cod)" intermediate, which is immediately protonated by the pyridinium group to regenerate

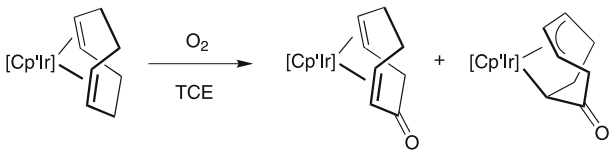


**Scheme 10**

the $\kappa^3$-bpa ligand with formation of the "$Rh^{III}$(hydroperoxo)(cod)" complex. Then, one oxygen atom is transferred to the C = C bond, while the fate of the other oxygen atom is unknown [72].

### 3.1.5
### Radical-chain Processes Involving Ketone Derivatives

Radical-chain processes that are usually operative in the auto-oxidation of free cod [73] can produce olefin oxygenation in some instances. This is the case of the reaction of [Ir($\eta^5$-Cp′)(cod)] (Cp′ = 3,5-$(Me_3Si)_2$Cp) [74] with dioxygen in tetrachloroethane (TCE) under reflux, where a free-radical chlorine-photosensitized oxidation gave two isomeric ketones (Eq. 18).



**Equation 18**

The setereochemistry of the products isolated in this reaction is related to that of the hydroperoxides produced in autoxidation of free cod.

### 3.1.6
### Electron-transfer Reactions Promoting $O_2$ Activation

An elegant illustration of this feature was provided by the reactivity of the redox-pair [$Rh^I$($\kappa^3$-dpa)(cod)]$(PF_6)$/[$Rh^{II}$($\kappa^3$-dpa)(cod)]$(PF_6)_2$ towards dioxygen [75]. The reluctance of the $Rh^I$ complex to react with dioxygen

is overcome by a one-electron oxidation process affording the paramagnetic $Rh^{II}$ complex. This compound, upon treatment with dioxygen, gives a rhodium superoxide complex (Fig. 3) in a reversible fashion. However, the superoxide complex does not transfer oxygen to the coordinated diolefin (cf. the binuclear oxygen activation and formation of C – O bonds discussed above), but rather it decomposes through a C – H bond activation reaction.

Another perhaps more relevant example consists of the redox pair $[Ir^{I}(\kappa^4\text{-}Me_3tpa)(C_2H_4)](PF_6)/[Ir^{II}(\kappa^4\text{-}Me_3tpa)(C_2H_4)](PF_6)_2$ [76]. In this case, while the reaction of the $Ir^{I}$ compound with oxygen affords the olefin-peroxide complex $[Ir(\kappa^3\text{-}Me_2dpa\text{-}Me)(O_2)(C_2H_4)](PF_6)$, as mentioned above, the product of the reaction of the paramagnetic Ir(II) complex with dioxygen in acetonitrile is the diamagnetic formylmethyl complex, $[Ir(\kappa^4\text{-}Me_3tpa)(\kappa^1\text{-}CH_2CHO)(MeCN)](PF_6)_2$ (Scheme 11) [77, 78]. The radical character of the complex $[Ir^{II}(\kappa^4\text{-}Me_3tpa)(C_2H_4)](PF_6)_2$ centered on the non-innocent ethylene ligand could be responsible for facile C – O bond formation, through the collapse of the C-centered radical in $[Ir(\kappa^4\text{-}Me_3tpa)(C_2H_4)](PF_6)_2$ [78] with dioxygen, which is a biradical by itself.

This observation opens up a new possibility in the formation of C – O bonds for the already complicated oxygenation reactions of organic substrates, i.e., the non-innocent behavior of the olefin in open-shell transition metal olefin complexes can allow a direct radical coupling of dioxygen with the coordinated olefin.

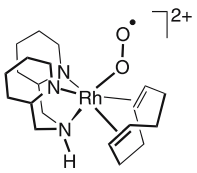
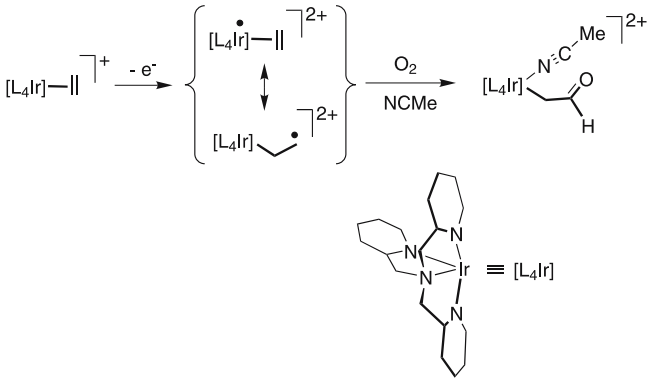



**Fig. 3**




**Scheme 11**

## 3.2
## Reactions with Hydrogen Peroxide

Hydrogen peroxide is the second environmentally friendly reagent of choice to be used as primary oxidant, since after the transfer of one of the oxygen atoms water is the only by-product. While oxygen is very selective in producing the oxygenation of the olefins coordinated to rhodium and iridium, hydrogen peroxide is more efficient for this purpose. For example, 2-rhoda$^{III}$oxetanes derived from ethylene (Fig. 4), inaccessible from the reactions of the appropriate precursors with dioxygen, are easily obtained if aqueous hydrogen peroxide is used instead [67, 79, 80].

The greater effectiveness of hydrogen peroxide is also shown in the reactions of the pentacoordinated complexes $[M(\kappa^3\text{-}L_n)(cod)]^+$ supported by N-donor ligands ($L_n$ = dpa-R′ [72, 79], Cn* [79], $Py_3S_3$ [81]) (Fig. 5). While these complexes are unreactive with molecular oxygen, they react with $H_2O_2$ to systematically give the 1-hydroxy-2-metalla$^{III}$(5,6,7)-allyl derivatives (Scheme 12) as the thermodynamic products.

These 1-hydroxy-2-metalla$^{III}$(5,6,7)-allyl complexes result directly from the reactions of the less sterically crowded complexes [Ir(Cn)(cod)](OTf) (Cn = 1,4,7-triazacyclononane) [82] and $[Rh(\kappa^3\text{-}Py_3S_3)(cod)](BPh_4)$ [81]. Slowing down the reactions by increasing the steric crowding around the metal, the kinetic isomers 2-irida$^{III}$oxetane and 6,7-oxarhoda$^{III}$tetracyclodecane can be isolated from the reactions of [Ir(Cn*)(cod)](OTf) [82] and $[Rh(\kappa^3\text{-}L_n)(cod)](PF_6)$ ($L_n$ = Cn*, dpa-R′) [72, 79] with $H_2O_2$, respectively. The

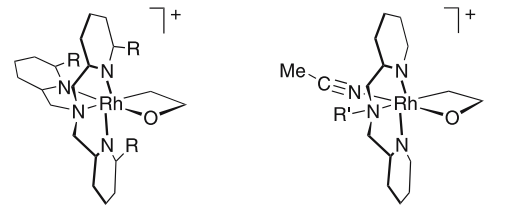



**Fig. 4**

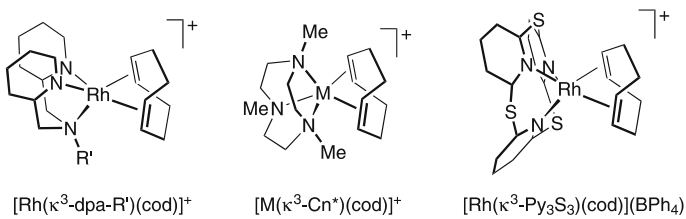
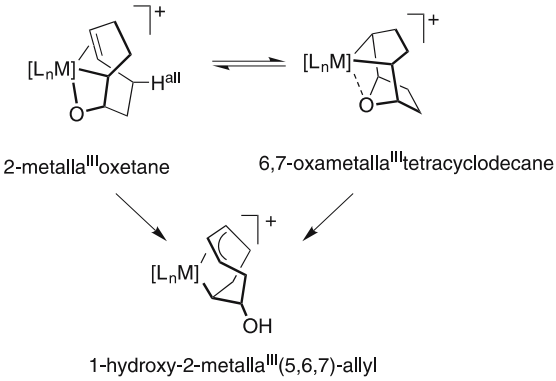



**Fig. 5**

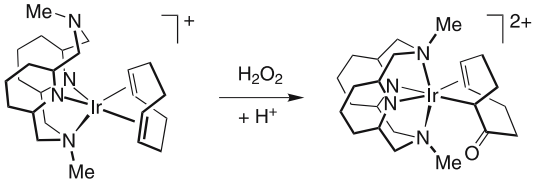



**Scheme 12**

unique organic fragment in the 6,7-oxarhoda$^{III}$tetracyclodecanes bonded to rhodium can formally be considered as a tetrahydrofuran derivative. This organic moiety may result from an internal attack of the oxygen atom to the closer olefinic carbon in a preceding 2-rhoda$^{III}$oxetane compound. Both types of oxametallacycles are transformed into the thermodynamic products, the 1-hydroxy-2-metalla$^{III}$(5,6,7)-allyl derivatives, on heating or through acid-catalyzed reactions. The conversion of the 2-irida$^{III}$oxetane is again regioselective (Sect. 3.1.3)

The conversion of the 6,7-oxarhoda$^{III}$tetracyclodecanes into the 1-hydroxy-2-metalla$^{III}$(5,6,7)-allyl products is more complicated since it involves the rupture of Rh – C and C – O bonds in the rhodium complexes. In some instances, an equilibrium between both types of complexes, 6,7-oxarhoda$^{III}$-tetracyclodecanes and 2-rhoda$^{III}$oxetanes, has been proposed to account for these results [72].

The only exception to this general trend, to date, is the reaction of the pyridophane iridium compound [Ir($\kappa^3$-dpda-$Me_2$)(cod)]($PF_6$) with hydrogen peroxide that requires the addition of one molar-equivalent of a strong acid to proceed. The acid not only protonates one arm of the ligand as an intermediate step, but it is consumed to produce the oxidation of the C = C bond to ketone. The product is the complex [Ir($\kappa^4$-dpda-$Me_2$)($\kappa^2$-$C_8H_{11}O$)]($PF_6$)$_2$ [83], containing a cyclooct-5-en-2-yl-1-one ligand, in a net four-electron oxidation (Eq. 19).




**Equation 19**

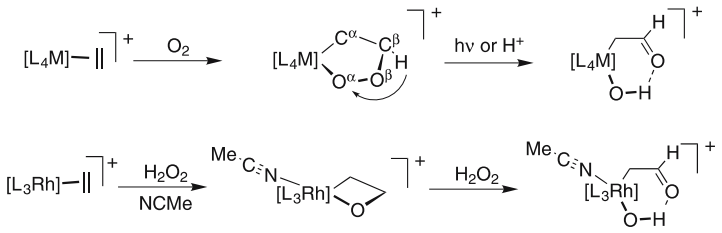
### 3.3
### Reactions of Dioxolane and Oxetane Complexes

The few 3-metalla$^{III}$-1,2-dioxolane complexes of rhodium and iridium isolated so far have been highly reactive species. Simply by exposure to daylight they rearrange to the very unusual formylmethyl hydroxy complexes [M($\kappa^4$-tpa)M(OH)($\eta^1$-$CH_2CHO$)](X) and [Rh($\kappa^4$-dpda-$Me_2$)(OH)($\eta^1$-$CH_2CHO$)]($PF_6$) in the solid state (Scheme 13) [84]. An alternative route to these formylmethyl hydroxy complexes is the oxidation of a 2-rhoda$^{III}$oxetane with hydrogen peroxide [67] (Scheme 13).

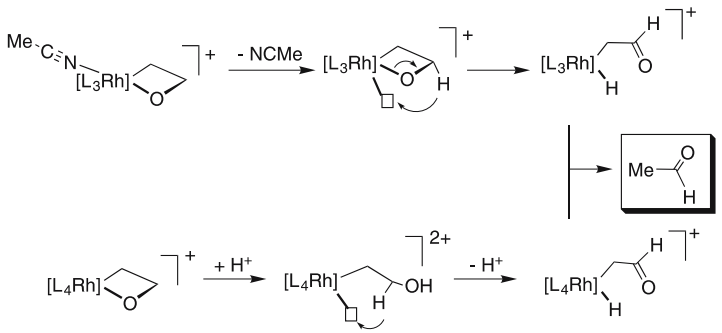
These formylmethyl hydroxy compounds could be intermediates [66] in the formation of acetaldehyde, for example, by the direct protonation of the $CH_2$ group by an external acid. Unfortunately, these formylmethyl hydroxy compounds do not eliminate acetaldehyde but, to the contrary, strong acids protonate the hydroxy group to give the aqua complex while the formylmethyl ligand remains unaltered.

However, the elimination of acetaldehyde from 2-rhoda$^{III}$oxetanes (Scheme 14) is observed if a coordination vacancy on the metal, necessary for a $\beta$-hydrogen elimination, is created. This is achieved by dissociation of an acetonitrile ligand [67] or by protonation [80] of the oxetane moiety.

The $\beta$-hydride shift followed by a reductive elimination produces acetaldehyde, while the resulting $Rh^I$ fragment is trapped by cod or ethylene to give




**Scheme 13**




**Scheme 14**

the $Rh^{I}$ compounds $[Rh(\kappa^3\text{-dpa-Bn})(L)](BPh_4)$ (L = cod, ethylene), respectively.

This $\beta$-hydrogen elimination in 2-rhoda$^{III}$oxetanes is apparently favored over reductive elimination to an epoxide. Moreover, the reverse step, i.e., the oxidative-addition of epoxides to $Rh^{I}$ and $Ir^{I}$ results in 2-rhoda$^{III}$oxetanes [85] and/or hydrido formylmethyl complexes [86]. Therefore, assuming that 2-metalla$^{III}$oxetanes are intermediates in the oxygenation of alkenes by group VIII transition metals, the reported reactivity would account for selectivity to ketones in the catalytic reactions based on these metals.

### 3.4
### A Close Look at Alkene Oxygenation Reactions

The recent advances described above confirm the feasibility of oxygenating olefins by oxygen and hydrogen peroxide in rhodium and iridium chemistry. This is not a common reaction of the olefinic complexes of these metals, nor are the products—mainly 2-metalla$^{III}$oxetane and 3-metalla$^{III}$-1,2-dioxolane complexes—that were isolated under solid-gas reactions, common products. On the whole, it represents an outstanding advance in the knowledge of the oxidation of olefins mediated by rhodium and iridium; transforming this stoichiometric into catalytic chemistry is a desired goal for the future. Nevertheless, several questions related to the activation and transfer of oxygen to the olefin remain unanswered, and the rationalizations given below should be taken as speculative proposals. For instance, what are the characteristics of the Rh and Ir olefin complexes that produce their effective interaction with dioxygen or hydrogen peroxide? Are there active oxygenated intermediate species? If the answer to the latter question is yes, then what makes them active and how does this occur? Also, in this context, how is the oxygen transferred to the alkene? Is there more than one reaction path?

It can generally be assumed that oxygen adds to $d^8$ $Rh^{I}$ and $Ir^{I}$ complexes in an oxidative way to form peroxocomplexes. While this reaction is usually reversible for rhodium, iridium peroxo complexes are more stable to dissociation [87]. By combining this reversibility, which is typical of rhodium, with electron-rich metal centers, which can be created by strong electron-donating ancillary ligands, one can expect square-planar 16-*e* metal complexes to be the most appropriate candidates for olefin oxygenation. $[Rh(\kappa^2\text{-}PhN_3Ph)(cod)]$ and $[Ir(\kappa^3\text{-}P_3O_9)(cod)](TBA)_2$, which are neutral and anionic coordinatively unsaturated complexes, fall into this category. In the iridium complex one Ir – O bond is very long (2.70 Å) while the other two are quite shorter (2.18 Å) [74], so that the existence of the coordinatively unsaturated $[Ir(\kappa^2\text{-}P_3O_9)(cod)](TBA)_2$ species in solution seems to be more than probable. Dissociation of one ligand or protonation of one arm of the ligand in pentacoordinated 18-e rhodium complexes with polydentate ligands

described by de Bruin and Gal is another way of achieving a coordination vacancy. However, the addition of dioxygen to the metal cannot be predicted a priori, and olefin replacement is a possible side reaction.

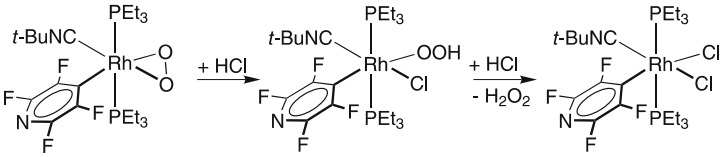
Once the oxidative-addition reaction of dioxygen to metal $d^8$-ions has occurred, the essentially electrophilic dioxygen becomes a nucleophilic peroxide ligand. Since the oxidation of substrates is associated with electron transfer from the substrate to the oxidant, i.e. in this case the dioxygen adduct, effective oxygenations require a "further activation" to transform the nucleophilic peroxide into an electrophilic species prior to the oxygen transfer.

It may be reasonable to argue that this "further activation" is achieved in several ways. The acid-catalysis required for Gal and de Bruin complex [Rh($\kappa^3$-bpa)(cod)]($PF_6$) to react with dioxygen can be used to protonate the peroxo compound (Scheme 10) to a hydroperoxo species. This is a way to achieve "further activation" of dioxygen, since it decreases the nucleophilic character of the peroxo ligand and makes interaction with the coordinated olefin easier. Recent works by Moro-oka [88, 89] and Braun [90] (Scheme 15) have shown that peroxorhodium complexes can be protonated to hydroperoxo compounds. However, the addition of a second mole of acid leads to hydrogen peroxide elimination rather than to the highly electrophilic oxo species (M = O) that could result from the heterolytic cleavage of the O – O bond with removal of water.

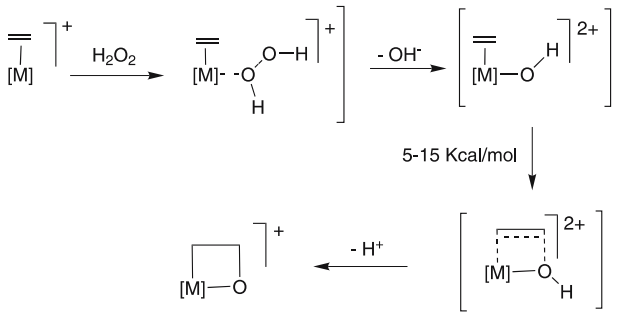
Oxo species (M = O) are almost unknown in Rh and Ir chemistry with the exception of the unique terminal iridium oxo complex, [Ir = O(mes)$_3$] (mes = 2,4,6-trimethylphenyl) [91]. This compound surprisingly displays little reactivity towards organic substrates, despite its high formal oxidation state. It only oxidizes the most reactive oxygen acceptors such as phosphanes or arsanes [92].

A second way to activate the peroxide ligand for oxygen transfer to C = C bonds could be via homolytic O – O cleavage of the peroxide by coordination to a second metal center. From this point of view, the peroxide ligand is converted into the "[M($\mu$-O)]$_2$" moiety in which the oxide bridges are now electrophilic and then each oxygen atom from the "M$_2$($\mu$-oxo)$_2$" core is transferred to a close C = C bond in a *cis* position (Scheme 8). As this conclusion is based on only two reported examples, it should be taken as a working hypothesis.

A third possible way to carry out the addition of oxygen to C = C bonds involves paramagnetic metal complexes in which the unpaired electron resides




**Scheme 15**




**Scheme 16**

partly on the olefin ligand. In this case no coordination of dioxygen to the metal is required, but it can attack the olefin directly, with addition occurring as a result of the collapse of free-radicals.

Moving on to the reactions with hydrogen peroxide, a hydroperoxide complex could be also formed by a direct interaction of hydrogen peroxide with metal complexes [93]. The hypothesis of a common intermediate, the hydroperoxo species, could reasonably be assumed in some reactions of rhodium cyclooctadiene complexes carried out with both $H_2O_2$ and $O_2/H^+$, since they gave identical products [72]. However, a DFT study [94] indicates that the heterolytic cleavage of the O – O bond by rhodium is most probably the first step in the oxygenation of ethylene with hydrogen peroxide (Scheme 16). The product, a 2-rhoda$^{III}$oxetane complex would result from an intramolecular nucleophilic attack of the hydroxide group on the coordinated olefin followed by the loss of the proton.

The low values found for the barriers associated with the heterolytic cleavage and cyclisation steps are the main reasons for considering this proposal to be valid.

Finally, it should be pointed out that unknown paramagnetic species are also obtained in some of these reactions, thus complicating the mechanistic panorama of the oxygenation of organic substrates.

## 4 Conclusions

The last 5 years have witnessed important advances and breakthroughs in the rhodium and iridium chemistry involved in olefin oxygenation and alcohol oxidation (dehydrogenation). After promising results in the 1980s with rhodium-based catalysts for alkene oxygenation there followed a long period of "hibernation". However, rhodium has recently re-emerged as a promising candidate for allylic oxidation of alkenes and to promote C – O bond formation reactions. The outstanding stoichiometric chemistry of alkene oxy-

genation developed recently evidences the need to search for new systems that are able to activate dioxygen with efficient transfer to alkenes. A deeper understanding of the as yet poorly known operating mechanisms and further reactivity studies directed toward discovering the appropriate reductive-elimination steps also needs to be acquired before achieving the desired goal of transforming this stoichiometric into catalytic chemistry.

Moreover, the already known ability of iridium compounds to catalyze hydrogen transfer reactions has been excellently applied in Oppenauer-type and domino-type reactions for valuable organic chemicals; and further developments, including asymmetric variants to kinetic resolution of alcohols and fine chemicals, can be expected.

Since these are still early days in our understanding of these aspects of rhodium and iridium, whether or not they are "rough diamonds" for these reactions is a question to be answered in the future.

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